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In Search for New Bonding Modes of the Methylenedithiolato Ligand: Novel Tri- and Tetra-metallic Clusters

R. S. Anju,[a] Koushik Saha,[a] Bijan Mondal,[a] Thierry Roisnel,[b] Jean-François Halet [b] and Sundargopal Ghosh[a],*

Building upon our earlier results on the chemistry of dirutheniunm analogue of pentaborane (9) with heterocumulenes, we continued to investigate the reactivity of *arachno*-$[(Cp^*Ru)_2(B_3H_8)(CS_2H)]$, **1**, ($Cp^* = \eta^5$-$C_5Me_5$) towards group 7 and 8 transition metal carbonyl compounds under photolytic and thermolytic conditions. The metal carbonyl compounds show diverse reactivity pattern with *arachno*-**1**. For example, the photolysis of *arachno*-**1** with $[Re_2(CO)_{10}]$ yielded $[(Cp^*Ru)_2B_3H_5(CH_2S_2)\{Re(CO)_4\}_2]$, **2**, $[(Cp^*RuCO)_2(\mu$-$H)_2(CH_2S_2)\{Re(CO)_4\}\{Re(CO)_3\}]$, **3** and $[(Cp^*Ru)_2(\mu$-$CO)(\mu$-$H)(CH_2S_2)\{Re(CO)_3\}]$, **4**. The geometry of **2** with a nearly planar eight-membered ring containing heavier transition metals rhenium, ruthenium is unprecedented. Compounds **3** and **4** can be considered as M_4-quadrilateral and M_3-triangle with a methylenedithiolato ligand attached to the metal centres respectively. $[Mn_2(CO)_{10}]$, on the other hand, reacts with *arachno*-**1** to yield heterometallic binuclear $[(Cp^*RuCO)\{Mn(CO)_4\}(\mu$-$H)(SCH_3)]$, **5** and homocubane $[(Cp^*Ru)_2\{Mn(CO)_3\}$-$(CS_2H_2)B_3H_4]$, **6**. In an attempt to generate group 8 analogues of **2**-**5**, we performed the reaction of *arachno*-**1** with $[Fe_2(CO)_9]$ and $[Ru_3(CO)_{12}]$. Although, the objective of isolating analogous compounds was not achieved, the reaction of $[Fe_2(CO)_9]$ led to novel tetrahedral cluster $[(Cp^*RuCO)\{(Fe(CO)_3\}_2S(\mu$-$H)]$, **7**. $[Ru_3(CO)_{12}]$, in contrast, yielded known compounds $[\{Cp^*Ru(CO)\}_2B_2H_6]$, **9** and $[Cp^*Ru(CO)_2]_2$, **10**. All the cluster compounds have been characterized by mass spectrometry, IR, and ^1H, ^{11}B, and ^{13}C NMR spectroscopy, and the geometric structures were unequivocally established by crystallographic analysis of **2**-**5** and **7**.

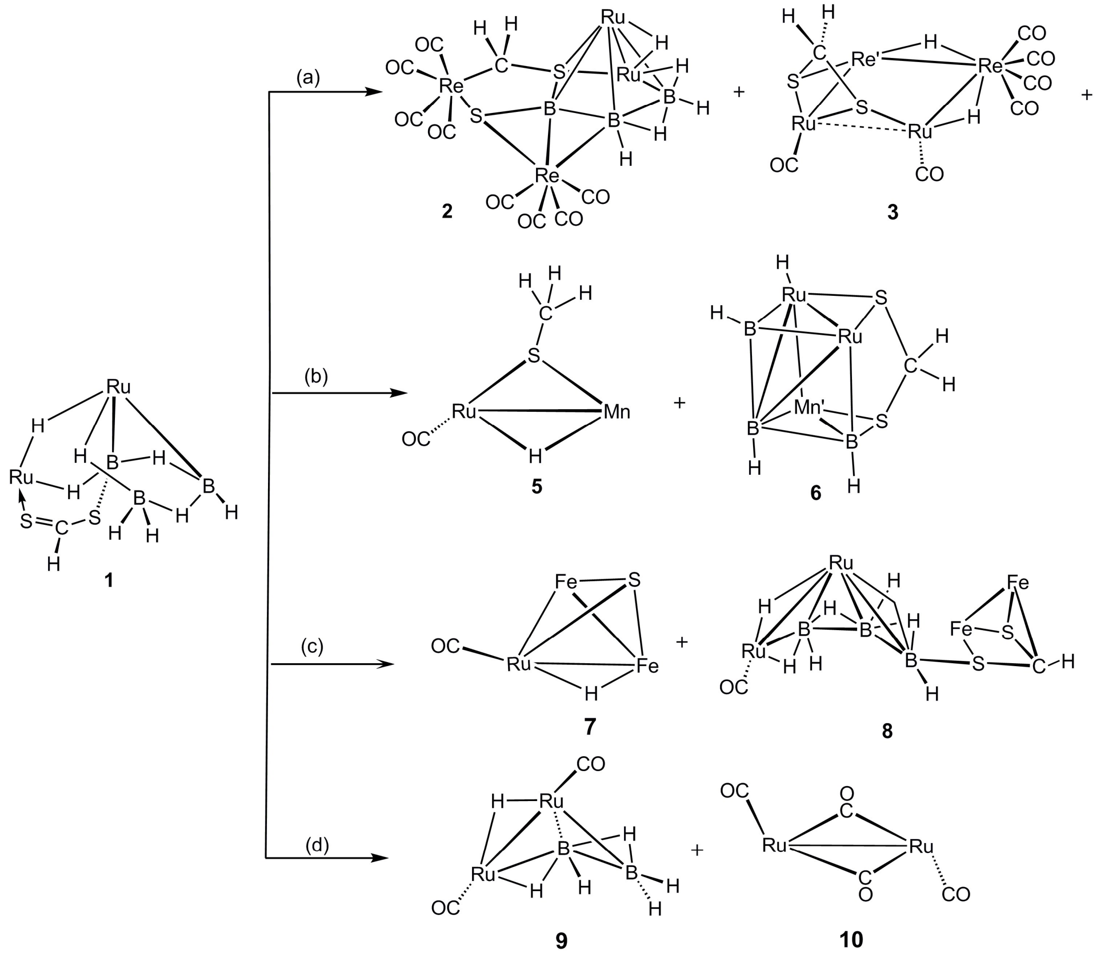
Introduction

The fascinating aspect of metallaborane chemistry is its close connection with organometallic chemistry.[1] The classic development in metallaborane chemistry begins with the finding of a new compound types and proceeds through synthetic improvements and structural development to systematic examination of reactivity.[1-5] This includes various approaches such as condensation reactions involving various monoborane reagents, insertion or fragmentation using borane or metal carbonyl fragments and intercluster fusion reactions.[1-5] In each case, reaction often leads to the formation of a wide range of products with different metal-to-boron ratios.

As part of our current research interest on the chemistry of polyhedral-boron clusters, we have recently reported the reactivity of heterocumulene ligands with *nido*-[1,2-$(Cp^*Ru)_2(\mu$-$H)_2B_3H_7]$ that resulted in the formation of *arachno*-$[(Cp^*Ru)_2(B_3H_8)(CS_2H)]$, **1** containing a dithioformato ligand.[6] Further, the chemistry of *arachno*-**1** adduct was explored with the first row transition-metal carbonyl compounds, such as, $[Fe_2(CO)_9]$ and $[Mn_2(CO)_{10}]$; and we have demonstrated that *arachno*-**1** offered a diverse reactivity pattern both under photolytic and thermolytic conditions to generate novel clusters. The dithioformato ligand played a key role in generating these uncommon geometries. The existence of such unique bonding types of dithoformato ligand prompted us to extend the chemistry of *arachno*-**1** with other early and late metal carbonyl compounds. Here in, in this article, we report the synthesis and structural characterization of a heterometallic cluster consisting of a nearly planar 8-membered ring along with unprecedented M_4 and M_3-type clusters.

Results and discussion

As shown in Scheme 1, the room temperature photolysis of **1** with $[Re_2(CO)_{10}]$ yielded compounds **2**-**4**. Although **2**-**4** are produced in a mixture, they can be separated by preparative thin-layer chromatography (TLC), allowing characterization of pure materials. Details of spectroscopic and structural characterization of **2**-**4** using IR, ^1H, ^{11}B, ^{13}C NMR, mass spectrometry and X-ray diffraction studies are given below.



Scheme 1. Synthesis of **2-10** ((a) [Re$_2$(CO)$_{10}$]: hν/THF/2 h; (b) [Mn$_2$(CO)$_{10}$]: 100 °C/Toluene/42 h; (c) [Fe$_2$(CO)$_9$]: hν/THF/4 h; (d) [Ru$_3$(CO)$_{12}$]: 100 °C/Toluene/8 h; Ru = Cp*Ru, Re′ = Re(CO)$_3$, Mn = Mn(CO)$_4$, Mn′ = Mn(CO)$_3$, Fe = Fe(CO)$_3$.

[(Cp*Ru)$_2$B$_3$H$_5$(CH$_2$S$_2$){Re(CO)$_4$}$_2$], 2: Compound **2** was isolated as an air stable orange solid in 21 % yield. The ^{11}B NMR spectrum of **2** shows three resonances at δ = 30.3, 11.9 and -17.5 ppm. The ^{1}H NMR spectrum of **2** displays the presence of two different types of Cp* ligands and high field resonances for the bridging protons. The IR and ^{13}C NMR suggest the presence of CO ligands. Crystal structure of **2**, shown in Fig. 1, shows a virtually planar eight membered ring comprising of transition metals and main group elements. A Cp*Ru unit is bonded to the five membered metalloheterocycle {S2-Ru3-B24-B23-B22} in a μ_5 fashion. Although the bond distances within the ring are not uniform, all the interatomic distances are found to be in the range of normal single bond. One of the two {Re(CO)$_4$} fragments in **2** is “externally” anchored to the eight-membered ring in μ_3-fashion generating a butterfly-like framework.

The presence of an approximately planar eight-membered ring in **2** demands further comments. There have been reports for the existence of compounds containing such planar rings that contain boron as a constituent. For example, the triple decker complexes such as [(Cp*ReH)$_2$B$_5$Cl$_5$][7] and [(Cp*Re)$_2$B$_6$H$_4$Cl$_2$][8] possess a completely planar B$_5$ and B$_6$ ring respectively. In a recent past, Fehlner reported a diruthenium organoborane [(Cp*Ru)$_2$(B$_8$H$_{14}$)],[9] analogous to binuclear pentalene complexes [(Cp*M)$_2$(C$_8$H$_6$)] (M = Fe, Ru),[10] that contains a planar B$_8$ moiety. The eight-membered ring of **2** is slightly puckered with dihedral angle of 6.04° between the mean planes of the rings S2-Ru3-B24-B23-B22 and S2-C21-Re1-S1-B22. The sp^3 hybridized carbon atom (C21) in **2** adopts a tetrahedral geometry and lays 0.503 Å above the plane containing Re1-S1-B22-S2. This, in turn, contributes maximum to the perturbation of planarity. This scenario is similar to that in [(η^5C$_5$H$_5$Cr)$_2${μ-η^6:η^6-(μ-1,2-C$_3$H$_6$-1,2-C$_2$B$_4$H$_4$)}], **I**, where a planar B$_4$C$_5$ ring is present with a dihedral angle of 4.53° between the planes containing the 6-membered and 5-membered rings.[11]

Similarly, [{η^5-C_5H_5Co}$_2${μ-η^5:η^5-(μ-1,2-C_3H_4-1,2-$C_2B_3H_3$)}], **II**, displays a planar C_2B_3 ring sandwiched between two CpCo fragments with an unsaturated {-CH=CH-CH2-} fragment (Chart 1).[12] Apart from this, [{η^5-C_5Me_5Re}$_2${μ-η^6:η^6-$B_4H_4Co_2(CO)_5$}][13] and [(Cp*Mo)$_2${μ-η^6:η^6-B_3H_3Te-$Co_2(CO)_5$}][14] possess 6-membered metallacycles that show considerable deviation from the planarity. Although, 8-membered ring systems containing lighter elements of the periodic table are known, such a system possessing a planar array of heavier transition metals and main group elements is unprecedented.

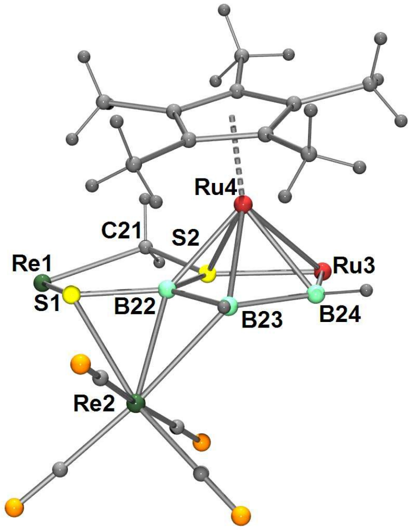
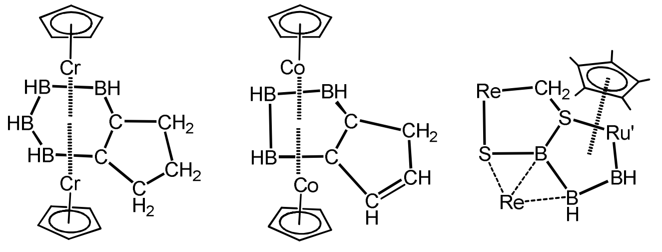


Fig. 1. Molecular structure and labeling diagram for **2** (Cp* ligand on Ru3 and the carbonyl ligands on Re1 are omitted for clarity and the complete structure has been given in Fig. S7). Selected bond lengths (Å) and bond angles (°): Re1-C21 2.246(4), Re1-S1 2.5378(10), B22-B23 1.721(6), Ru3-B24 2.363(5), S1-B22 1.846(5), Re2-B23 2.573(5), Ru3-Ru4 2.8523(4), Ru4-B22 2.196(5), S1-B22 1.846(5); B22-Re2-S1 44.12(11), B22-Re2-B23 40.52(15).



I **II** **2**

Chart 1. Selected compounds with 8-membered planar hetero-ring systems (In compound 2, Re = Re(CO)$_4$; Ru′ = Cp*Ru and bridging hydrogens are not shown for clarity)

To gain some insight into the structure and bonding nature of **2**, we carried out the density functional theory (DFT) calculations[15] and compared with [(Cp*Ru)$_2$(B_8H_{14})] (Fig. S1 and Fig. S3).[9b,16] The optimized structure (Table S1) and calculated NMR chemical-shift values (^{1}H and ^{11}B) of **2** closely resemble those measured experimentally (Table S2). The DFT calculations were helpful in locating the accurate positions of the bridging hydrogen atoms. A HOMO-LUMO gap of 2.0 eV is computed for **2**, indicating it's thermodynamic stability (Table S3). Interestingly, the HOMOs are mostly localized on the planar and "unsaturated" part of the cluster (Fig. 2 and Fig. S2) which is metallic in character.

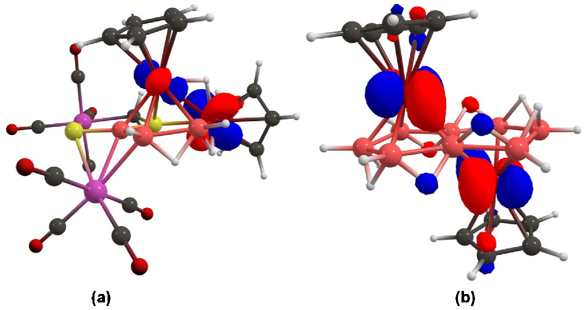


Fig. 2. Highest Occupied Molecular Orbital (HOMO) of (a) **2** and (b) [(CpRu)$_2$(B_8H_{14})].

M$_4$ and M$_3$ clusters:

Compound **3** was isolated after chromatographic separation, as brown and air-stable solid in 10% yield. The solid-state structure of **3** obtained from the crystallographic analysis, (Fig. 3) exhibits a heterometallic M$_2$M′$_2$ quadrilateral consisting of two ruthenium and two rhenium atoms with a methylenedithiolato ligand acting as a bridge between three metal atoms (Ru1, Ru2, and Re1). The geometry of **3** can be related to that of [$Os_4(CO)_{16}$] with one missing M-M bond.[17] The three interatomic bonding distances (Ru1-Re3 3.341 Å; Re3-Re2 3.331 Å; Re2-Ru2 2.918 Å) between the metals are in the larger limit of the reported M-M single bonds.[18] Compound **3** possesses 66 valence electrons (Ru (8) x 2 + Re (7) x 2 + Cp* (5) x 2 + (CO) (2) x 9 + μ-H (1) x 2 + SCH$_2$S (6) x 1); whereas a metallic square cluster contains 64 valence electrons. One can account for the presence of two extra electrons in **3** due to the absence of a direct M-M bond. Thus, structure of **3** is consistent with the electron counting rules.[19]

The NMR, mass spectrum and microanalysis data unequivocally support the solid-state structure of **3**. The ^{1}H NMR spectrum shows sharp resonances for two metal-bridging hydrides at δ = -17.1 and -14.2 ppm along with the peaks corresponding to two distinct Cp* ligands. The ^{13}C and IR spectra confirm the presence of CO groups.

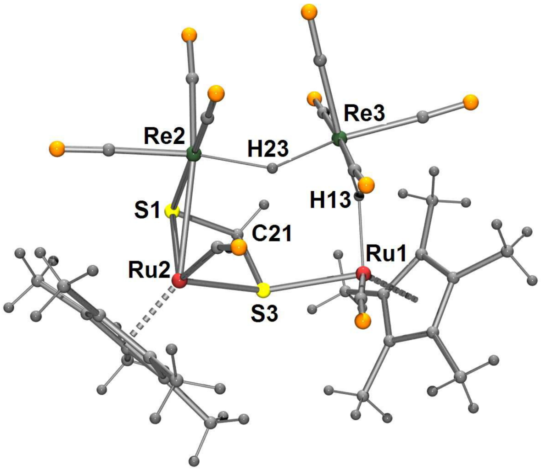


Fig. 3. Molecular structure and labeling diagram for **3**, selected bond lengths (Å) and bond angles (°): S1-Ru2 2.376(3), S1-Re2 2.437(3), S3-Ru1 2.390(2), S3-Ru2 2.418(2), Ru2-Re2 2.9179(8), Re2-H23 1.89(6), Re3-H13 1.84(2), Re3-H23 1.88(6), C21-S1 1.834(10), C21-S3 1.841(10); S1-Re2-Ru2 51.73(7), Ru2-Re2-H23 87(4), S3-Ru2-Re2 94.32(6).

Compound **4** was isolated as green moisture sensitive solid in 9 % yield. The mass spectrum of **4** gave a molecular ion peak at 849, corresponding to the formula of $C_{25}H_{33}O_4S_2Ru_2Re$. The IR spectrum displayed bands at 1820 and 1991 cm^{-1} due to bridging and terminal CO groups, respectively. Both the ^1H and ^{13}C NMR spectra of **4** are consistent with the presence of a σ-plane of symmetry. The ^1H NMR spectrum showed a single signal at $\delta = 1.7$ ppm indicating the presence of one type of Cp* ligand. Presence of a hydrido and methylenedithiolato ligands were confirmed by ^1H NMR spectrum. Further, to elucidate the structure of compound **4**, a single crystal X-ray analysis was undertaken.

The crystals suitable for analysis were grown from concentrated hexane solution at ambient temperature. The solid-state molecular structure of **4** (Fig. 4) displays a hetero-trimetallic M_2M' triangle[20] with a methylenedithiolato ligand bridged among the three metals in an unusual symmetrical fashion. A σ-mirror plane passing through C21-Re1-C22 divides the molecule into two equal halves. The Cp* ligands attached to the ruthenium metal are eclipsed to each other. Unlike **3**, all the intermetallic distances in **4** correspond to 'normal' single bond lengths. Based on the electron counting rules, a metallic triangle containing three M-M bonds is expected to possess 48 valence electrons.[21] The total number of valence electrons available in **4** is indeed 48 (13 (Cp*Ru) x 2 + 13 ($Re(CO)_3$) + 2 (μ-CO) + 6 (SCH_2S) + 1 (μ-H).

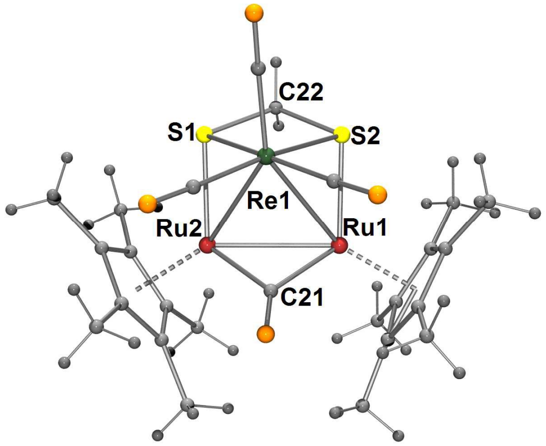


Fig. 4. Molecular structure and labeling diagram for **4**, selected bond lengths (Å) and bond angles (°): S1-Ru2 2.360(3), S1-Re1 2.480(3), S2-Ru1 2.348(3), S2-Re1 2.466(3), Ru1-Ru2 2.7767(13), Ru1-Re1 2.9585(10), Ru2-Re1 2.9626(11), C22-S2 1.831(12), C22-S1 1.817(12); Ru1-C21-Ru2 85.4(4), S1-C22-S2 104.7(6), Ru2-S1-Re1 75.44(9), Ru1-S2-Re1 75.79(9).

Although Re and Mn belongs to the same triad, we failed to isolate the manganese analogue of **2**. Thus, to verify the accessibility of the manganese analogue of **2**, quantum chemical calculations were performed on $[(CpRu)_2B_3H_5(CH_2S_2)\{Mn(CO)_4\}_2]$, **2a** (a hypothetical combination of ruthenium and manganese, Fig. S4). The DFT-MO study indicates a HOMO-LUMO gap of 1.91 eV for **2a**, similar to that computed for **2** (2.0 eV), indicating that compound **2a** is thermodynamically stable and a synthetically potential target (Table S3 and Fig. S5). This led us to reinvestigate the reaction of **1** with $[Mn_2(CO)_{10}]$ under various reaction conditions. As a result, we reinvestigated the reaction of *arachno*-**1** with $[Mn_2(CO)_{10}]$. Although, the objective of synthesising the manganese analogue of **2** was not achieved, thermolysis of **1** with $[Mn_2(CO)_{10}]$ resulted in the formation of a hetero-metallic binuclear sulphide complex $[(Cp^*Ru)CO\{Mn\ (CO)_4\}(\mu\text{-}H)(SCH_3)]$, **5**. Note that, the photolysis of **1** in presence of $[Mn_2(CO)_{10}]$ did not lead to any new compounds.[6]

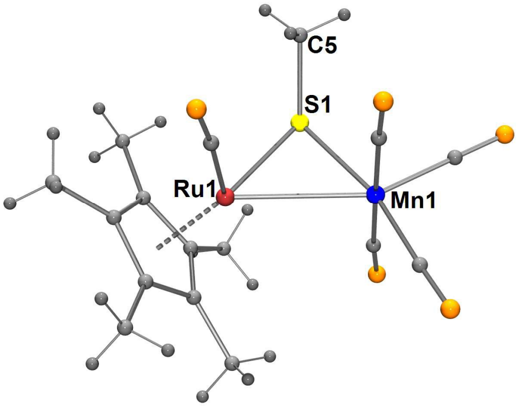


Fig. 5. Molecular structure and labeling diagram for **5**, selected bond lengths (Å) and bond angles (°):C5-S1 1.804(8), S1-Mn1 2.3142(19), S1-Ru1 2.3257(18), Mn1-Ru1 2.8683(10); S1-C5-H5A 109.5, Mn1-S1-Ru1 76.36(6), S1-Ru1-Mn1 51.64(5), S1-Mn1-Ru1 52.00(5).

In order to confirm the spectroscopic assignments and to determine the full molecular and crystal structure of **5**, an X-ray analysis was undertaken. The crystal structure of **5** corresponds to discrete molecules of $[(Cp^*Ru)CO\{Mn\text{-}(CO)_4\}(\mu\text{-}H)(SCH_3)]$ separated by normal van der Waals distances (Fig. 5). It shows the existence of a simple triangle composed of two metal atoms and a main-group element. The Ru1-Mn1 distance of 2.8683(10) Å in **5** is slightly longer as compared to the previously reported compounds derived from **1** and $[Mn_2(CO)_{10}]$.[6] This is probably due to the presence of the bridging hydride ligand present between Ru1 and Mn1. Both Ru1-S1 and Mn1-S1 interatomic distances are in the range of normal single bonds. Although a large number of bimetallic sulphido compounds have been reported in literature,[22] most of them contain a disulphide linkage, as observed for $[CpMoMn\text{-}(CO)_5(\mu\text{-}S_2)]$,[23] $[\{Mn(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}S_2)]$[24] and $[Mn(CO)_3\text{-}CpNi(\mu\text{-}S_2)]$[25] or two sulphide ligands as in the case of $[Cp^*M(PMe_3)(\mu\text{-}S)_2M'(NO)Cp^*]$[26] (M = Rh, Ir; M′ = Mo, W).[27] Except few, complexes with a single sulphide bridged between two metal atoms are rare (Chart 2),[28] in particular, complexes only with a mono-sulphide bridge between ruthenium and manganese.[22]

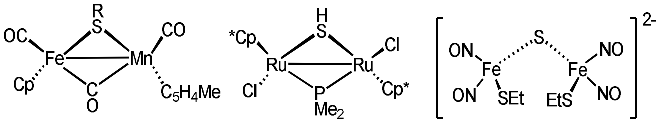


Chart 2. Selected bimetallic complexes containing single sulphide unit

In an attempt to synthesise group 8 metal carbonyl analogues of **2**, we carried out the reaction of group 8 transition metal carbonyl compounds with **1**. Unfortunately, none of our attempts led to the isolation of analogous 2-4. The room temperature photolysis of **1** in presence of $[Fe_2(CO)_9]$ for 4 hours yielded tetrahedral compound $[Cp^*RuCOFe_2(CO)_6(\mu\text{-}H)]$, **7**, along with heterometallic *exo*-polyhedral cluster $[(Cp^*Ru)_2(B_3H_8)(CO)\{Fe(CO)_3\}_2(CS_2H)]$, **8** (Scheme 1).[6] The molecular structure, relevant bond angles and bond lengths of **7** are given in the supporting information (Fig. S6). Further, the reaction of **1** with $[Ru_3(CO)_{12}]$ was examined[29] that yielded known *arachno*-$[(Cp^*Ru(CO)_2B_2H_6]$[30] and $[Cp^*Ru\text{-}(CO)_2]_2$[31] under thermolytic and photolytic conditions.

Conclusion

This report describes the isolation and structural characterization of an unprecedented planar 8-membered metallathiacycle comprising of heavier transition metals and a main group element. In parallel to this, novel M_2M_2'-quadrilateral and M_2M'-triangle (M = Ru and M′ = Re) organometallic systems with methylenedithiolato ligands have been structurally characterised. A comparative reactivity of $[(\mathrm{Cp^*Ru})_2(\mathrm{B_3H_8})(\mathrm{CS_2H})]$ with group 7 and group 8 transition metal carbonyl compounds demonstrates the significance of the transition metals in determining the molecular geometry of clusters.

Experimental Section

General Procedures and Instrumentation. All manipulations were conducted either under an atmosphere of dry argon inside a glove box or by employing standard Schlenk techniques. Solvents were distilled prior to use under argon. Compound **1** was prepared according to literature method,[6] while other chemicals $[\mathrm{Cp^*RuCl_2}]_2$, $\mathrm{LiBH_4{\cdot}THF}$, $[\mathrm{Re_2(CO)_{10}}]$, $[\mathrm{Mn_2(CO)_{10}}]$, $[\mathrm{Fe_2(CO)_9}]$ and $[\mathrm{Ru_3(CO)_{12}}]$ were obtained commercially and used as received. The external reference for the ^{11}B NMR, $[\mathrm{Bu_4N(B_3H_8)}]$ was synthesized according to literature method.[32] Thin layer chromatography was carried on 250-mm diameter aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 or 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as reference (δ, ppm, d$_6$-benzene, 7.16, $\mathrm{CDCl_3}$, 7.26), while a sealed tube containing $[\mathrm{Bu_4N\text{-}(B_3H_8)}]$ in d$_6$-benzene (δ_B, ppm, −30.07) was used as an external reference for the ^{11}B NMR. The infrared spectra were recorded on a Nicolet iS10 spectrometer. MALDI-TOF mass-spectra of the compounds were obtained on a Bruker Ultraflextreme using 2,5-dihydroxybenzoic acid as a matrix and a ground steel target plate. The photoreactions described in this report were conducted in a Luzchem LZC-4V photoreactor, with irradiation at 254−350 nm. Microanalyses for C and H were performed on PerkinElmer 2400 Series II CHNS/O elemental analyzer.

Synthesis of 2-4. In a flame-dried Schlenk tube, the purple solution of *arachno*-**1** (0.50 g, 0.84 mmol) and three equivalents of $[\mathrm{Re_2(CO)_{10}}]$ in THF (15 mL) was irradiated for 2 h. The volatile components were removed under vacuum and the residue was extracted into hexane and passed through celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a hexane/$\mathrm{CH_2Cl_2}$ (90:10 v/v) mixture yielded orange **2** (0.22 g, 21.7%), brown **3** (0.10 g, 10.0%) and green **4** (0.08 g, 9.2%). **2**: MS(MALDI): m/z 1183 M^+, isotope envelope. $\mathrm{C_{29}H_{37}B_3O_8S_2Ru_2Re_2}$ requires 1184.7163; ^{11}B NMR (22 °C, 128 MHz, $\mathrm{CDCl_3}$): $\delta = 30.3$ (s, 1B), 11.9 (s, 1B), -17.5 (s, 1B); ^{1}H NMR (22 °C, 400 MHz, $\mathrm{CDCl_3}$): $\delta = 5.3$ (br, 1H, $\mathrm{BH_t}$), 4.8 (br, 1H, $\mathrm{BH_t}$), 2.5 (s, 2H, $\mathrm{CH_2}$), 1.9 (s, 15H, $\mathrm{Cp^*}$), 1.8 (s, 15H, $\mathrm{Cp^*}$), 0.9 (br, B-H-B), -6.4 (br, Ru-H-B), -11.5 (s, Ru-H-Ru), -12.2 (br, Ru-H-B); ^{13}C NMR (22 °C, 100 MHz, $\mathrm{CDCl_3}$): $\delta = 192.4$(s, CO), 187.2 (s, CO), 93.0 (s, $C_5\mathrm{Me}_5$), 90.2 (s, $C_5\mathrm{Me}_5$), 29.3 (s, $\mathrm{CH_2}$), 10.2 (s, $\mathrm{C}_5\mathit{Me}_5$), 9.7(s, $\mathrm{C}_5\mathit{Me}_5$); IR (hexane, cm^{-1}): 2553 ($\mathrm{BH_t}$), 2500 ($\mathrm{BH_t}$), 2423 ($\mathrm{BH_t}$), 1994 (CO), 1930 (CO); Elemental analysis calcd (%) for $\mathrm{C_{29}H_{37}B_3O_8S_2Ru_2Re_2}$: C, 29.40; H, 3.14; found: C, 29.74; H, 3.00; **3**: MS(MALDI): m/z 1148 [M^+-CO], isotope envelope. $\mathrm{C_{30}H_{34}O_9S_2Ru_2Re_2}$ requires 1177.2696; ^{1}H NMR (22 °C, 400 $\mathrm{Cp^*}$), -14.2 (s, 1H, Re-H-Re), -17.1 (s, Re-H-Ru); ^{13}C NMR (22 °C, 100 MHz, $\mathrm{CDCl_3}$): $\delta = 201.1$ (s, CO), 198.2 (CO), 190.1 (s, CO), 186.2 (s, CO), 100.0 (s, $C_5\mathrm{Me}_5$), 98.1 (s, $C_5\mathrm{Me}_5$), 24.7 (s, $\mathrm{CH_2}$), 13.2 (s, $\mathrm{C}_5\mathit{Me}_5$), 12.9 (s, $\mathrm{C}_5\mathit{Me}_5$); IR (hexane, cm^{-1}): 1991 (CO), 1980 (CO), 1957 (CO), 1949 (CO); Elemental analysis calcd (%) for $\mathrm{C_{30}H_{34}O_9S_2Ru_2Re_2}$: C, 30.60; H, 2.91; found: C, 30.00; H, 3.01; **4**: MS(MALDI): m/z 849 [M^+], isotope envelope. $\mathrm{C_{25}H_{33}O_4S_2Ru_2Re}$ requires 850.0041; ^{1}H NMR (22 °C, 400 MHz, $\mathrm{CDCl_3}$): $\delta = 2.6$ (s, 2H, $\mathrm{CH_2}$), 1.7 (s, 30H, $\mathrm{Cp^*}$), -17.9 (s, 1H, Ru-H-Ru); ^{13}C NMR (22 °C, 100 MHz, $\mathrm{CDCl_3}$): $\delta = 201.3$ (s, CO), 198.9 (s, CO), 96.0 (s, $C_5\mathrm{Me}_5$), 23.2 (s, $\mathrm{CH_2}$), 10.2 (s, $\mathrm{C}_5\mathit{Me}_5$); IR (hexane, cm^{-1}): 1991 (CO), 1820 (CO); Elemental analysis calcd (%) for $\mathrm{C_{25}H_{33}O_4S_2Ru_2Re}$: 35.32; H, 3.91; found: C, 35.01; H, 3.78.

Synthesis of 5. In a flame-dried Schlenk tube, the purple solution of *arachno*-**1** (0.50 g, 0.84 mmol) and two equivalents of $[\mathrm{Mn_2(CO)_{10}}]$ in toluene (15 mL) was thermolysed at 100 °C for 42 h. The volatile components were removed under vacuum and the residue was extracted into hexane and passed through celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a hexane/$\mathrm{CH_2Cl_2}$ (90:10 v/v) mixture yielded yellow **5** (0.04 g, 9%) and **6** (0.19 g, 30.8%). **5**: MS(MALDI): m/z 465 [M^+-CO], isotope envelope. $\mathrm{C_{16}H_{34}O_5SMnRu}$ requires 494.5112; ^{1}H NMR (22 °C, 400 MHz, $\mathrm{CDCl_3}$): $\delta = 2.1$ (s, 3H, $\mathrm{CH_3}$), 1.9 (s, 15H, $\mathrm{Cp^*}$), -14.7 (s, 1H, Ru-H-Mn); ^{13}C NMR (22 °C, 100 MHz, $\mathrm{CDCl_3}$): $\delta = 197.2$ (s, CO), 187.9 (s, CO), 101.3 (s, $C_5\mathrm{Me}_5$), 22.1 (s, $\mathrm{CH_2}$), 12.8 (s, $\mathrm{C}_5\mathit{Me}_5$); IR (hexane, cm^{-1}): 1977 (CO), 1991 (CO); Elemental analysis calcd (%) for $\mathrm{C_{16}H_{34}O_5SMnRu}$: C, 38.86; H, 6.93; found: C, 38.75; H, 6.49.

Synthesis of 7. In a flame-dried Schlenk tube, a purple solution of *arachno*-**1** (0.50 g, 0.84 mmol) and two equivalents of $[\mathrm{Fe_2(CO)_9}]$ in THF (20 mL) was irradiated for 4 h at room temperature. The volatile components were removed under vacuum and the residue was extracted into hexane and passed through celite. After removal of solvent, the residue was subjected to chromatographic work-up using silica gel TLC plates. Elution with a mixture of hexane/$\mathrm{CH_2Cl_2}$ (80:20 v/v) yielded brown **7** (0.06g, 12.2%) and **8** (0.19 g, 34.4%). **7**: MS(MALDI): m/z 579 [M^+], isotope envelope. $\mathrm{C_{17}H_{19}O_7SFe_2Ru}$ requires 580.1536; ^{1}H NMR (22 °C, 400 MHz, CDCl3): 1.7 (s, 15H; Cp*), -20.7 (s, 1H, Ru-H-Fe): ^{13}C NMR (22 °C, 100 MHz, CDCl3): δ = 100.9 (s, C5Me5), 13.5 (s, C5Me5); IR (hexane, cm-1): 1985 (CO), 1935 (CO).

Note that compounds **6** and **8** have been characterized by comparison of their spectroscopic data reported earlier.[6]

X-ray Structure Determination. The crystal data for **2-5** and **7** were collected and integrated using an APEXII Bruker-AXS diffractometer equipped with a CCD camera and a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation source at 150 K (**2**, **3** and **7**) and T = 273 K (**4** and **5**). The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97.[33,34]

Crystal data for 2. $\mathrm{C_{29}H_{34}B_3O_8Re_2Ru_2S_2}$, $M_r = 1181.65$, Monoclinic, $P2_1/c$, $a = 10.6073(2))$ Å, $b = 16.4222(4)$ Å, $c = 21.8033(4)$ Å, $\beta = 103.1730(10)$ °, $V = 3698.09(13)$ Å^3, $Z = 4$, F(000) = 2228, $R_1 = 0.0259$, $wR_2 = 0.0521$, 8383 independent reflections [$2\theta \leq 55.00$ °] and 432 parameters.

Crystal data for 3. $\mathrm{C_{30}H_{34}O_9Re_2Ru_2S_2}$, , $M_r = 1177.23$, monoclinic, $P2_1/n$, $a = 12.4115(3)$ Å, $b = 15.6418(4))$ Å, $c = 18.9999(4)$ Å, $\beta = 99.573(2)$ °, $V = 3637.24(15)$ Å^3, $Z = 4$, F(000) = 2224, $R_1 = 0.0498$, $wR_2 = 0.1264$, 6395 independent reflections [$2\theta \leq 50.00$ °] and 423 parameters.

Crystal data for 4. $\mathrm{C_{25.50}H_{33}ClO_4ReRu_2S_2}$, $M_r = 891.43$, orthorhombic, *P*bca, $a = 16.489(3)$ Å, $b = 18.360(4)$ Å, $c = 19.101(4)$ Å, $\beta = 90.00$ °, $V = 5783.0(2)$ Å^3, $Z = 8$, F(000) = 3440, R_1

= 0.0498, wR$_2$ = 0.1031, 5076 independent reflections [2θ≤50 °] and 345 parameters.

Crystal data for 5. $C_{16}H_{18}MnO_5RuS$, M$_r$ = 478.37, monoclinic, *P21/n*, *a* = 14.0465(7) Å, *b* = 9.2479(4) Å, *c* = 15.2684(5) Å, *β* = 104.888(4) °, *V* = 1916.79(14) Å^3, *Z* = 4, F(000) = 956, R$_1$ = 0.0556, wR$_2$ = 0.1347, 3757 independent reflections [2θ≤51.98 °] and 224 parameters.

Crystal data for 7. $C_{17}H_{16}Fe_2O_7RuS$, M$_r$ = 577.13, monoclinic, *C2/c*, *a* = 19.1610(6) Å, *b* = 8.4810(2) Å, *c* = 26.7034(7) Å, *β* = 111.4380(10) °, *V* = 4039.19(19) Å^3, *Z* = 8, F(000) = 2288, R$_1$ = 0.0380, wR$_2$ = 0.0770, 4620 independent reflections [2θ ≤ 53.8 °] and 262 parameters.

Computational details. All calculations were performed with no symmetry constraints at the density functional theory (DFT) level with the Gaussian 09 package[15] using the BP86 functional.[35] The basis set 6-311+G(2d,p) employed for C, H, B, O and S atoms and a Couty & Hall's modified LANL$_2$DZ effective core potential basis set[36] augmented by a polarization function for the *p* valence orbitals for ruthenium and rhenium.[37] Harmonic vibrational frequency calculations were performed to check that the optimized geometries were energy minima. The NMR chemical shifts were computed at the B$_3$LYP level of theory by using the approximation of the gauge-including atomic orbital (GIAO)[38] method implemented in Gaussian 09. The δ(^{11}B) and δ(^{1}H) chemical shifts were referenced to $F_3B{\cdot}OEt_2$ and TMS, respectively. For the NBO[39,40] and population analysis, the BP86 functional and a 6-31G(d) basis set were employed. Wiberg bond indexes (WBI)[41] were obtained from a natural bond orbital (NBO) analysis. Multiwfn 3.1 was used for the topological analyses of the electron densities.

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Notes and references

[a] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India. E-mail: sghosh@iitm.ac.in; Fax: (+91) 44 2257 4202; Tel: (+91) 44 2257 4230

[b] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, F-35042 Rennes Cedex.

CCDC 1031974-1031978 contain the supplementary crystallographic data for compounds **2-5** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.1 or other electronic format see DOI: 10.1039/b000000x/

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In Search for New Bonding Modes of the Methylenedithiolato Ligand: Novel Tri- and Tetra- metallic Clusters

R. S. Anju,[a] Koushik Saha,[a] Bijan Mondal,[a] Thierry Roisnel,[b] Jean-François Halet[b] and Sundargopal Ghosh[a,]*

[a] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India.

E-mail: sghosh@iitm.ac.in; Fax: (+91) 44 2257 4202; Tel: (+91) 44 2257 4230

[b] Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, F-35042 Rennes Cedex.

Photolysis of *arachno*-[$(Cp^*Ru)_2(B_3H_8)(CS_2H)$] in presence of [$Re_2(CO)_{10}$] produced [$(Cp^*Ru)_2B_3H_5(CH_2S_2)\{Re(CO)_4\}_2$], with a planar 8-membered ring containing heavier transition metals and a main group element.